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THE NATURE OF THE SYSTEM (π-$C_4H_7PdCl)_2$–ELECTRON DONOR FROM ^1H, ^{13}C AND ^{31}P NMR SPECTROSCOPIC AND ELECTRODIALYSIS STUDIES

III. (π-$C_4H_7PdCl)_2$–DIMETHYLSULFOXIDE

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SUMMARY

The interaction between DMSO and crotyl- or allyl-palladium halides involves a downfield shift of all the absorption lines in the ^{13}C NMR spectra, with the signal due to DMSO also being shifted downfield. Investigations of the temperature and concentration dependence of the electrical conductivity together with electrodialysis studies of the complex $(^{14}C_4H_7Pd^{36}Cl)_2 + DMSO$ indicate that the downfield shift arises from a cleavage of the Cl^- ion and the formation of the cation $C_4H_7PdDMSO_2^+$.

The kinetic parameters of the exchange between DMSO and the complex have been evaluated.

INTRODUCTION

It has been shown[1] that the ^{13}C NMR spectra of allylpalladium chloride in dimethylsulfoxide (DMSO) solution differ from those measured in $CDCl_3$ solution in that the C_1, C_2 and C_3 absorption signals are shifted downfield. Similar shifts were also observed in the ^{13}C spectra of crotylpalladium halides.

The changes in the ^1H NMR spectra associated with the use of DMSO as a solvent have already been reported, the observed equivalence of the allyl-group methyl protons being accounted for by "rotation" of the protons of the σ-allyl compound formed in the reaction of the complex with the ligand[2].

On the basis of a simultaneous change in the ^1H NMR spectra and the electrical conductivity, it has been suggested that the spectrum of allylpalladium chloride in DMSO may be explained in terms of a rapid exchange of various complex species, including ionic species[3,4].

An attempt has been made in the present study to investigate in greater detail the dependence of the ^1H and ^{13}C NMR spectra and electrical conductivity of crotylpalladium chloride on the concentration of added DMSO and the temperature. The nature of the ions formed in the system has been investigated by electrodialysis experiments using samples of the complex in which both the allyl group and chloride were labelled, *i.e.* $(^{14}C_4H_7Pd^{36}Cl)_2$.

EXPERIMENTAL

Electrodialysis of the complex was carried out in a three-cell dialyzer divided by membranes; a given amount of the "labelled" complex was placed in the centre cell and, after switching on the power, samples were withdrawn from the cathode, anode and central cells at definite time intervals using a microsyringe.

Radioactivity measurements were made using a Beckman LS-250 liquid scintillation spectrometer.

The technique used to obtain the NMR spectral measurements has already been described in Part II of this series[8].

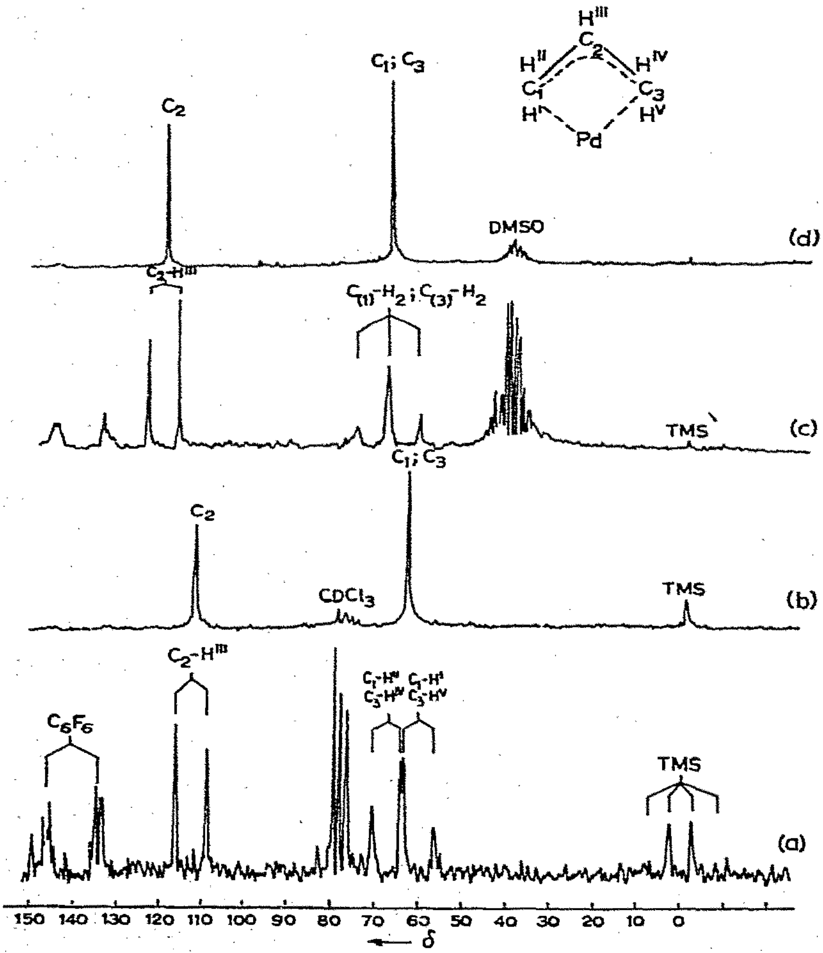


Fig. 1. The ^{13}C NMR spectrum of allylpalladium chloride. (a) $(\pi\text{-}C_3H_5PdCl)_2$ in $CDCl_3$; (b) $(\pi\text{-}C_3H_5PdCl)_2$ in $CDCl_3$ as obtained with broad-band decoupling; (c) $(\pi\text{-}C_3H_5PdCl)_2$ in DMSO; (d) $(\pi\text{-}C_3H_5PdCl)_2$ in DMSO as obtained with broad-band decoupling.

RESULTS AND DISCUSSION

The ^{13}C NMR spectrum of allylpalladium chloride in $CDCl_3$ (Fig. 1a) consists of an asymmetric quartet at δ 62.8 ppm and a doublet at δ 111 ppm (the exact parameter values of the spectra being given in Fig. 1). The quartet corresponds to absorption of C_1 and C_2 equivalent nuclei with H^I, H^{II}, H^V and H^{IV} splitting whilst the doublet corresponds to equivalent C_2 nuclei with H^{III} splitting. Use of broad-band decoupling transforms the spectrum into two singlets, with shifts occurring exactly in the centre of gravity of the corresponding multiplets (Fig. 1b).

The addition of DMSO to the $CDCl_3$ solution of the complex results in the whole spectrum being shifted downfield (with the C_1 and C_3 signals shifting to a greater extent), the extent of the shift being proportional to the concentration of added ligand (Fig. 2).

Using DMSO-d_6 as the solvent results in both the downfield shift and the shift between individual signals attaining a maximum value; the absorption signal attributable to C_1+C_3 is transformed from a quartet into a symmetric triplet ($J(^{13}C\text{–}H)$ 161 Hz), the lines being broadened as a result of H^I, H^{II}, H^{IV} and H^V proton exchange (see description of the ^1H NMR spectrum under similar conditions[2]). The doublet lines attributable to the C_2 nuclei remain narrow, but when spin–spin decoupling is utilized (Fig. 1d) the spectrum is transformed into two singlets.

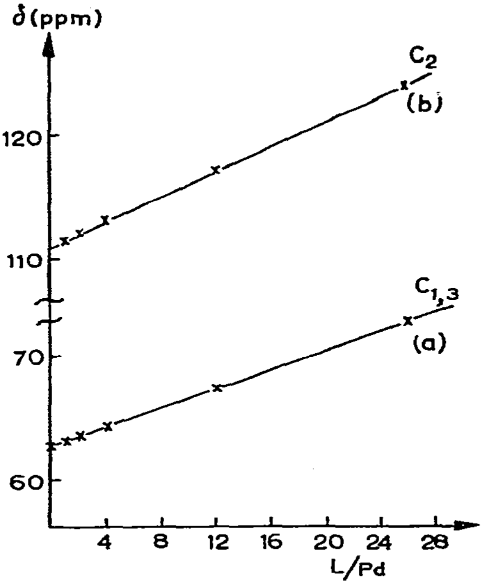


Fig. 2. (a) $C_{1,3}$ and (b) C_2 chemical shifts in the ^{13}C NMR spectrum of allylpalladium chloride in $CDCl_3$ as a function of the DMSO concentration.

The spectrum of (π-$C_4H_7PdCl)_2$ in $CDCl_3$ (Fig. 3a) consists of four groups of signals, *i.e.*, a symmetric quartet at δ 18.4 ppm due to the CH_3 group, an asymmetric triplet due to the CH_2 group (δ 58.4 ppm) and two doublets at δ 81.6 ppm (C_3) and at δ 111.6 ppm (C_2) which, in turn, are further split due to long-range ^{13}C–C–H coupling

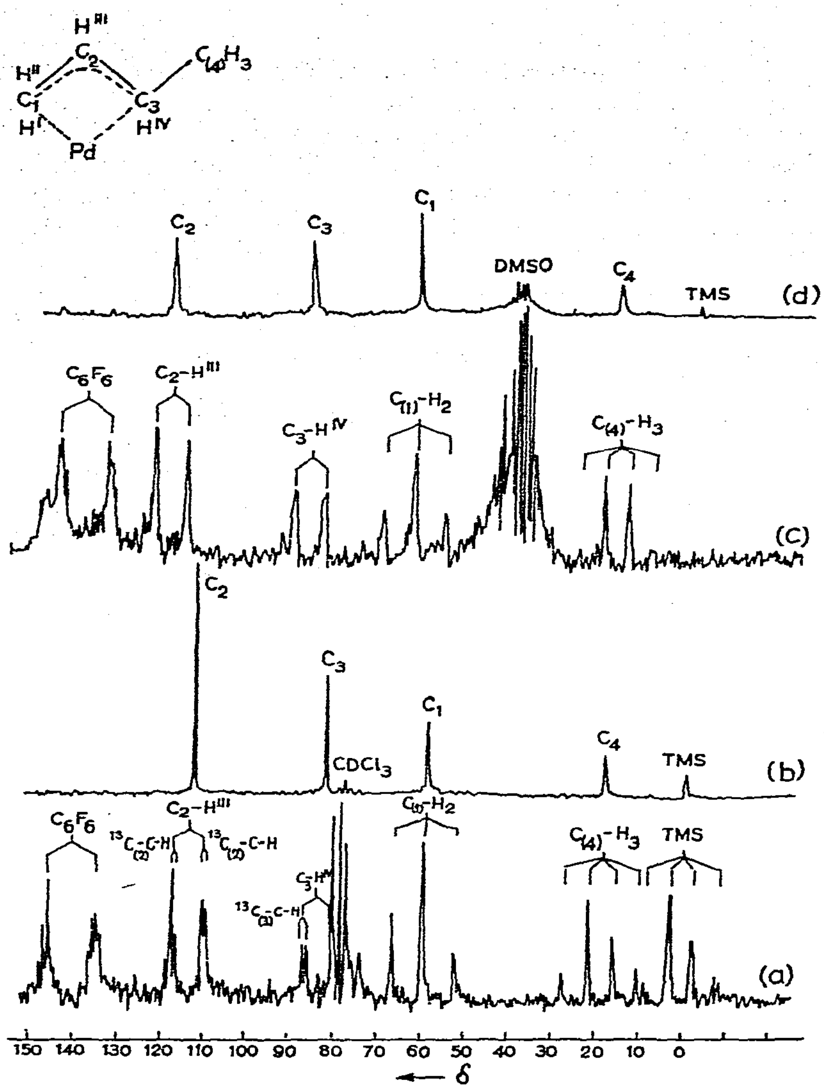


Fig. 3. The ^{13}C NMR spectrum of crotylpalladium chloride. (a) $(\pi\text{-}C_4H_7PdCl)_2$ in $CDCl_3$; (b) $(\pi\text{-}C_4H_7PdCl)_2$ in $CDCl_3$ as obtained with broad-band decoupling; (c) $(\pi\text{-}C_4H_7PdCl)_2$ in DMSO; (d) $(\pi\text{-}C_4H_7PdCl)_2$ in DMSO as obtained with broad-band decoupling.

(an exact assignment of long-range coupling constants was not attempted).

The spectrum obtained with broad-band decoupling consists of four singlets, the shift being in the centre of the corresponding multiplets (Fig. 3b).

The NMR spectra of $(\pi\text{-}C_4H_7PdBr)_2$ and $(\pi\text{-}C_4H_7PdI)_2$ in $CDCl_3$ are similar to that of $(\pi\text{-}C_4H_7PdCl)_2$[1]. The position of the CH_3 group is little affected by the nature of the halogen (a downfield shift of 1.7 ppm occurs with $(\pi\text{-}C_4H_7PdI)_2$ in comparison to $(\pi\text{-}C_4H_7PdCl)_2$. Comparison of the series Cl, Br and I indicates that the C_3 carbon signal is shifted downfield by 6.2 ppm, the position of the central C_2 carbon

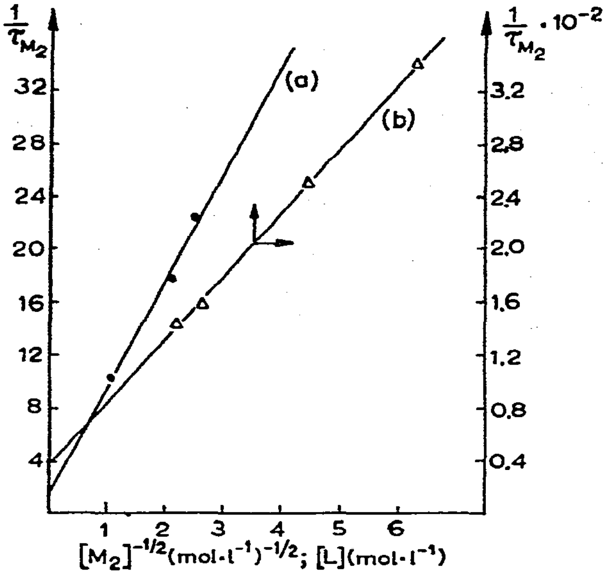


Fig. 4. Plots of $1/\tau_{M_2}$ (a) as a function of the DMSO concentration in $CDCl_3$ and (b) as a function of $(\pi\text{-}C_4H_7PdCl)_2^{-\frac{1}{2}}$ concentration in C_6H_6.

absorption being virtually independent of the nature of halogen and the same for allyl and crotyl groups in a given solvent.

On heating a solution of allylpalladium chloride in DMSO, the triplet attributable to the C_1+C_3 nuclei in the undecoupled spectrum narrows due to an increase in the exchange rate of the H^I, H^{II}, H^{IV} and H^V protons. Similarly, on heating a solution of crotylpalladium chloride in DMSO the broadened triplet attributable to the C_2 nuclei narrows with the simultaneous disappearance of the ^{13}C–C–H long-range coupling for the C_2 and C_3 nuclei which is clearly visible at 20°C in chloroform solution.

Heating allylpalladium chloride in DMSO also results in the absorption signals of nuclei $C_{1,3}$ and C_2 being slightly shifted upfield (~32 Hz).

Varying the concentration of DMSO (=L) at constant $(C_4H_7PdCl)_2$ (=M_2) concentration and varying the concentration of (M_2) at constant [L] indicates that the exchange rate is directly proportional to the concentration of DMSO (Fig. 4a) and to the square-root of the concentration of the dimer complex (Fig. 4b).

Of the possible kinetic schemes for ligand-complex interaction, the following were examined:

Case (A)

$$M_2+L \rightleftharpoons M_2L$$

Case (B)

$$M_2 \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} 2\,M \tag{1}$$

$$M+L \underset{k_{-2}}{\overset{k_{+2}}{\rightleftharpoons}} ML \tag{2}$$

Case (*C*)

$$M_2+L \rightleftharpoons ML+M$$

$$M+L \rightleftharpoons ML$$

Case (A), which suggests that $1/[M_2] \propto 1/\tau_{M_2}$, is not in agreement with the experimental observations.

These observations are, in fact, best explained in terms of case (B), provided that $v_{+2} \ll v_{-1}$ and that step +2 in the process is rate determining. Hence

$$-\frac{d[M_2]}{d\tau} = k_{+2}[L]\,[M] = \frac{1}{2}k_{+2}\cdot K_1^{\frac{1}{2}}\,[M_2]^{\frac{1}{2}}$$

where K_1 is the equilibrium constant for reaction (1), and therefore

$$\frac{1}{\tau_{M_2}} = \frac{1}{2}k_{+2}K_1^{\frac{1}{2}}[L][M_2]^{-\frac{1}{2}} \qquad (3)$$

When $L/Pd \ll 1$, the absorption signal due to DMSO in the ^1H NMR spectrum is shifted downfield. This shift decreases as the L/Pd ratio increases until at $L/Pd = 1$ it practically coincides with the shift of free DMSO. This suggests that (a) a rapid (on an NMR time scale) exchange occurs between the ligand and the complex over the whole concentration range and (b) the equilibrium lies significantly towards the free components.

Hence, combining equations (1) and (2) with the expression for the collapsed signal shift when rapid exchange occurs gives

$$\Delta L = \frac{K_2[M]}{1+K_2[M]}$$

or

$$\frac{1}{\Delta L} = \frac{1}{K_2\Delta ML}\cdot\frac{1}{[M]} + \frac{1}{\Delta ML}$$

where

$$\Delta L = \delta_{exp.} - \delta_L$$

$$\Delta ML = \delta_{ML} - \delta_{exp.}$$

But from equation (1). $[M] \simeq K_1^{\frac{1}{2}}\cdot[M_2]_0^{\frac{1}{2}}$

Therefore

$$\frac{1}{\Delta L} = \frac{1}{K_2\Delta ML} - \frac{1}{K_1^{\frac{1}{2}}\cdot[M_2]_0^{\frac{1}{2}}} + \frac{1}{\Delta ML} \qquad (4)$$

The dependence of $1/\Delta L$ on $[M_2]^{-\frac{1}{2}}$ is represented by the straight line in Figure 5, the intercept being equal to $1/\Delta ML$ and, hence, $\Delta ML = 50$ Hz. From the slope of this it has been found that $K_2\cdot K_1^{\frac{1}{2}} = 0.74$.

Although equation (4) does not enable a decision to be made between the schemes involving the formation of ML, it excludes case (A), for this would require $1/\Delta L$ to be proportional to $1/[M_2]$.

However, the relationship between the exchange kinetics and the collapsed

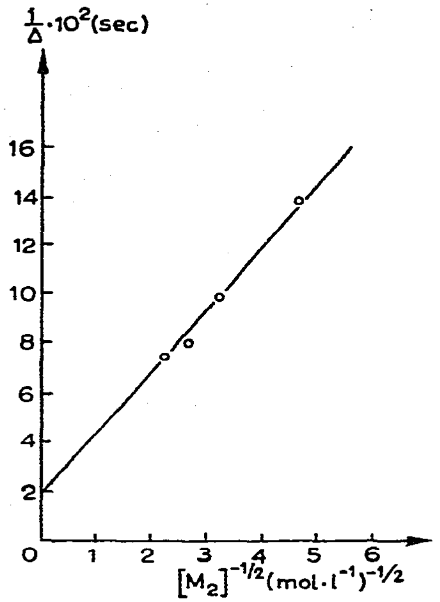
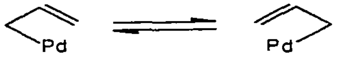


Fig. 5. A plot of ΔL^{-1} as a function of $[M_2]^{-\frac{1}{2}}$. Solvent C_6H_6; temperature 20°.

signal shifts suggests that case (B) is more consistent with the experimental data obtained.

These results do not agree with the conclusions reached by Mann *et al.*[6] who, on the basis of the ^{13}C NMR spectra of allylpalladium chloride, questioned the existence of the π-allylic structure, *i.e.* the structure with the electron density uniformly distributed between the three carbon atoms.

According to these authors, the experimental data may best be accounted for in terms of a rapid exchange involving two isomeric π, σ forms.



On the basis of this suggestion, the π-allyl chloride complex might be expected to be highly dissociated, yet our molecular weight measurements indicate that the complex is dimeric within the limits of experimental error. Indirect determination of K_1 gave a value of $\sim 10^{-3}$ mol/l in good agreement with the value of 4×10^{-3} mol/l found by Syrkin and co-workers[7].

Variation in temperature and in concentration of the complex should affect the rates of the processes. However, no changes in the ^{13}C and ^{1}H spectra (broadening and splitting of lines etc.) were observed as the temperature of a $(C_3H_5PdCl)_2$ solution in $CDCl_3$ was decreased to the freezing point.

The electrical conductivity of allylpalladium chloride in $CHCl_3$ at a constant complex concentration increases as the square of the concentration of DMSO added to the solution (Fig. 6a) and as the square-root of the complex concentration at a constant value of [L] (Fig. 6b). This suggests that the electrical conductivity arises from the dissociation of the monomeric species formed as a result of the decomposi-

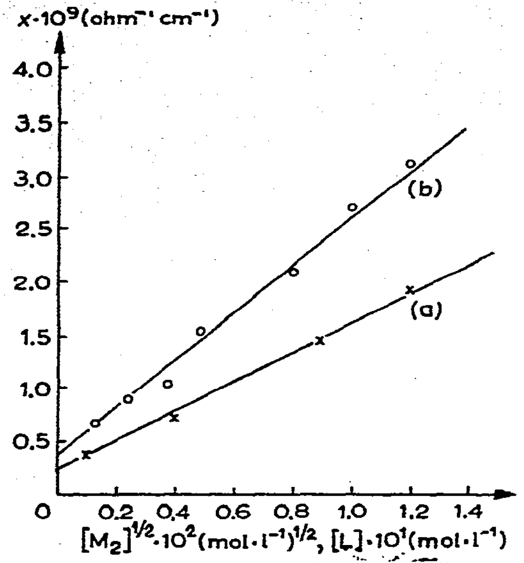


Fig. 6. The electrical conductivity of allylpalladium chloride as a function of (a) the DMSO concentration and (b) the absolute concentration of $(\pi\text{-}C_3H_5PdCl)_2^{\frac{1}{2}}$.

tion of bis(π-allylpalladium chloride) rather than from direct ionic dissociation of the complex.

The dependence of the electrical conductivity on $[L]^2$ in $CHCl_3$ solution suggests that before dissociation occurs a molecule of the complex adds approximately two atoms of DMSO.

To investigate the nature of the ions formed. electrodialysis studies were undertaken using a solution of the double-labelled complex, $(\pi\text{-}{}^{14}C_4H_7Pd^{36}Cl)_2$. Kinetic studies of the dialysis of this complex in DMSO solution demonstrated that the flow rates of ^{14}C and ^{36}Cl in both cells were practically identical at a given temperature.

From general considerations it follows that ion formation may result from cleavage of either a Pd–C or a Pd–Cl bond (equations (6) and (5) respectively),

$$\begin{tikzcd} {[RPdX]_2 + nL} \arrow[r, shift left] & RPdXL_n \arrow[l, shift left, "+L"] \arrow[r, shift left, "k_{+5}"] \arrow[d, shift right, "k_{+6}"'] & RPdL_n^+ + X^- \arrow[l, shift left, "k_{-5}"] & (5) \\ & R^- + PdXL_{n+1}^+ \arrow[u, shift right, "k_{-6}"'] & & (6) \end{tikzcd}$$

or from disproportionation of the complex:

$$[RPdX]_2 \overset{L_n}{\rightleftharpoons} [RPdL_n]^+ + [RPdX_2]^- \qquad (7)$$

The ratio of ^{13}C to ^{36}Cl measured experimentally and the fact that no Pd was found in the anode cell rule out the possibility of reaction (7).

When a toluene solution was used, the rate of ion diffusion decreased by two orders of magnitude at DMSO/Pd = 20, the concentration of ^{14}C in the cathode cell being one order of magnitude higher than that in the anode cell.

These results and the dependence of the electrical conductivity on $[L]^2$ under the conditions indicated above suggest that the main reaction in this case is reaction (5) with $n=2$.

For reaction (6) to be important, a high concentration of DMSO would be necessary, conditions which may only be achieved if DMSO is used as the solvent.

When excess (π-C_4H_7PdCl) is present, the absorption signal due to DMSO in the ^1H NMR spectra is shifted downfield due to complex formation and electron transfer to the palladium atom. As a result of this transformation the allyl group signal in the ^1H and ^{13}C NMR spectra is also shifted downfield, *i.e.* under these conditions the allyl group also acts as an electron donor, while the chloride ion appears to act as an electron acceptor.

The only reaction which can possibly give rise to such shifts is reaction (5) which involves cleavage of a chloride ion and the formation of the symmetric cationic allylic complex. Further increase in the concentration of DMSO favours reaction (6), the downfield shift of the resulting cationic complex signal being compensated by an allyl anion shift. Heating the complex in a DMSO solution results in an increase in the contribution of reaction (6) and gives rise to an upfield shift.

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